

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problems Mailbox.**

(19)



Eur päisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 965 411 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
22.12.1999 Bulletin 1999/51

(51) Int. Cl.⁶: **B23K 35/28**, B23K 35/36
// C22C18/04

(21) Application number: 99201563.6

(22) Date of filing: 19.05.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 22.05.1998 EP 98201710

(71) Applicant: HOOGOVENS STAAL B.V.
1970 CA IJmuiden (NL)

(72) Inventor: Van Veen, Johan Frank
1827 GT Alkmaar (NL)

(74) Representative:
Hansen, Willem Joseph Maria et al
Hoogovens Corporate Services BV,
Industrial Property Department,
P.O. Box 10000
1970 CA IJmuiden (NL)

(54) **Method of joining aluminium members to ferrous members, assembly of aluminium-ferrous members and the use of a pasty metal containing filler in such joining**

(57) Method of joining an aluminium member or a zinc-coated aluminium member to a ferrous member or to a zinc-coated ferrous member while applying a pasty metal containing filler in the joint region and thereupon heating of the pasty filler and subsequently cooling of the joint region, whereby the pasty filler contains 60 to 80 wt.% of a mixture of powdered metals, said mixture mainly comprising an aluminium-zinc alloy with a liquidus temperature below 419°C and containing aluminium in a range of 1.5 to 18 wt.%, the balance being zinc and impurities, the pasty filler further comprising 40 to 20 wt.% of an inorganic, fluorides containing flux material, and whereby the heating of the pasty filler is performed at a temperature below 430°C.

EP 0 965 411 A1

Description

[0001] The invention relates to a method for joining an aluminium member or a zinc-coated aluminium member to a ferrous member or a zinc-coated ferrous member using a pasty powder containing soldering filler, to an assembly of such joined members, and the invention further relates to the use of a pasty metal containing filler in such joining.

[0002] Within the scope of this invention aluminium is to be understood as to include aluminium alloys, for example aluminium alloys of the Aluminium Association AA1000, AA3000, AA5000, AA6000-series type. Zinc is to be understood as to include zinc alloys, in particular those zinc alloys known in the art for the use of electrolytic galvanised steel and/or aluminium. Ferrous is to be understood as to include steel, e.g. alloyed steel and low-carbon steel, and in particular steel alloys used in automotive and/or building applications. Members are to be understood as to include plate, sheet, extrusions, forgings, or shaped materials such as for example an automotive interior panel or exterior panel.

[0003] In the joining of aluminium members often the process of soldering and brazing are distinguished. Both processes employ a filler metal, which upon being melted, joins the members to be joined without melting these members. This opposed to the process of welding in which a substantial amount of the base metal of the members to be joined is melted.

[0004] Soldering and brazing distinguish by the liquidus temperature of the filler metal. In a brazing a high-melting filler metal is applied having a liquidus temperature above 450°C and below the solidus temperature of the base metal, whereas the solders used in soldering melt below 450°C, see ASM Specialty Handbook, Aluminium and Aluminium Alloys, ASM International, Materials Park, 3rd. printing, May 1994, p.420.

[0005] Usually aluminium members are brazed at temperatures ranging from 500 to 700°C in industrialised processes.

[0006] The joining of an aluminium or zinc-coated aluminium member to a ferrous or zinc-coated ferrous member has a potential use in construction applications, automotive applications, and domestic applications such as in cooking pans. In construction applications, e.g. roofing and facade constructions, the necessary soldering must be performed on site, and frequently in outdoor situations, and preferably under similar conditions and by applying similar techniques as are common in the craft of soldering metal members, e.g. soldering zinc sheets. In automotive applications the necessary soldering must be able to be performed in a (semi-) automated manner, and must be able to compete with joining techniques like buff-welding of members of the same type. The joining of an aluminium based member to a ferrous based member, of which one or both members might be coated with zinc, by means of butt-welding on an industrial scale still meets

several difficulties. An alternative joining technique is a subject of on-going research.

[0007] From US-A-5,322,205 a method is known for joining an aluminium member to a dissimilar metal member, excluding copper, by soldering through the use of a solder for said aluminium member, comprising the steps of plating a selected metal on a surface of said dissimilar metal member to be joined to said aluminium member, dipping said plated portion into a molten solder to form a layer of an intermetallic compound and an oxide on a surface of said plated portion, ultrasonically vibrating said plated portion while in said dipping state in said molten solder so as to peel off said layer of said intermetallic compound and said oxide together with said plating, thereby activating the surface of said dissimilar metal member and producing a wetting with the solder, and making the solder adhere to said activated surface of said dissimilar metal member. The use of flux is not necessary.

[0008] From EP-A-0785045 a pasty metal for soldering aluminium and aluminium alloys surfaces, comprising a filler, a binder and a flux, whereby said flux comprises the cesium fluoroaluminate reaction product of from about 30 to about 70 mole percent of CsF and from about 70 to about 25 mole percent of AlF_3 , wherein the flux has a melting point below about 440°C; and up to about 3 weight percent of unreacted CsF.

[0009] From DE-C-946405 a solder material for joining aluminium with steel is known, whereby the solder consists of an alloy of 70% zinc, 29.5% aluminium and 0.5% manganese and further a flux comprising of a mixture of 20 to 30% ZnCl_2 , 15 to 20% CaCl_2 , 30 to 40% KCl, 15 to 20% NaCl, 1.5% NaF and 3.5% KF.

[0010] From EP-B-0732983 a method is known for the production of large-area aluminium or aluminium-alloy plates to be fixed to iron-alloy workpieces, using a soldering paste consisting of a powder containing aluminium in a range of 80 to 90% and silicon in a range of 20 to 10 %, a flux containing approximately 50% potassium fluoride and approximately 50% aluminium fluoride, and further a binder. According to the known method first the soldering paste is sprayed on to the plate, dried and age-hardened. Subsequently the soldering paste is then fixed in second operation by spraying on the binder solution. A disadvantage of the known method of joining the two different metal type members is that it is a time consuming method dedicated for use in cooking ware, which method further includes multiple process steps. A further disadvantage of the known process is that the method cannot readily be applied on a construction site.

[0011] An object of the invention is to provide a method which is applicable under the described circumstances.

[0012] The method of the invention is characterised in that the known method of the introduction of the pasty filler contains 60 to 80 wt.% of a mixture of powdered metals, that said mixture mainly comprises an aluminium-zinc alloy with a liquidus temperature of below

419°C and that said alloy contains aluminium in the range of 1.5 to 18 wt.%, the balance being essentially zinc and impurities, that the pasty filler further comprises 40 to 20 wt.% of an inorganic, fluorides containing flux material and that further the heating of the pasty filler is performed at a temperature below 430°C.

[0013] In accordance with the method of the invention it is achieved that a pasty filler has been provided which enables to join an aluminium or a zinc-coated aluminium member to a ferrous or to a zinc-coated ferrous member. Applying the pasty filler can be done in a simple method, either manually or in an automated manner. Further it is achieved that the filler can be applied on a construction site, as well as in an industrial (semi-) automated manner. A further advantage is that in case at least one of members has a thin zinc coating, the thin zinc coating is not interrupted.

[0014] Suitable flux materials containing fluorides are known per se. For instance they have been described in EP-A-0355987. The composition of the flux material may be adapted case to case to the composition of the filler and to the use of zinc-coated or non-coated aluminium member and/or to the use of zinc-coated or non-coated ferrous member.

[0015] The pasty filler comprises 60 to 80 wt.% of the powdered aluminium-zinc alloy, preferably in the range 65 to 75 wt.% and more preferably in the range 67 to 72 wt.%, and 40 to 20 wt.% of the inorganic, fluorides containing flux. A particular blend of the flux comprises aluminium fluoride, potassium fluoride, or complexed with each other. Further, the inorganic flux comprises at least also the element cesium or salt complexes thereof. The flux may further comprise a paste vehicle, preferably conventional, e.g. solid grade poly-isobutylene.

[0016] More preferably the said aluminium-zinc alloy has a liquidus temperature in the range of 370-400°C, which means that melting of such an alloy already can be achieved well below 419°C, i.e. below the liquidus temperature of the zinc coating.

[0017] Because of the selected flux material the molten filler metal was found to be able to make a good joint when a zinc-coated member is used without disrupting said coating.

[0018] The best results for a good joint were found to be achievable by making use of an aluminium-zinc alloy containing aluminium in the range of 1.5 to 5.0 wt.%, and preferably in the range of 1.5 to 2.5 wt.%. An aluminium-zinc alloy having 2 wt.% aluminium has a solidus temperature of about 378°C and a liquidus temperature of 388°C. The metal powder used has preferably a nominal powdered filler metal mesh size passing U.S. Standard Sieve No. -100 +200.

[0019] It is clear that when a zinc coating is applied to the members that the thicker the zinc coating the more the soldering will be similar to the soldering of a zinc member. On the other end it was found to be preferable according to the invention that the zinc-coated aluminium members have a zinc coating with a weight in the

range of 10 to 300 g/m². In the embodiment where a zinc-coated ferrous member is used it has been found according to the invention that the zinc coating has preferable a weight in the range of 40 to 250 g/m².

[0020] In the embodiment where a zinc-coated member is used a strong joint is found also to depend upon the connection between the aluminium member and/or steel member and the zinc-coating. Best results were obtained in accordance with the invention if the zinc-coating is produced by electrolytic deposition, for example by a process for zinc-coated aluminium sheet material described in the international patent application no. WO-A-97/43467.

[0021] In the common soldering of for instance zinc sheets the method solder may flow into the joint, even if the non-melted solder is melted adjacent to the joint.

[0022] In the embodiment where the aluminium member is not zinc-coated, the members are preferably pretreated by means of etching. A preferred etching pretreatment includes first an etch in an alkaline environment, followed by an etch in an acidic environment. The etching pretreatment has been found to be particular useful in case the aluminium member is made of an AA5000-series aluminium alloy, more in particular for those having a magnesium content 3 wt.% or more.

[0023] In applying the new method it has been found to be advantageous if the pasty filler is applied between the members where the joint is to result. The best results have been obtained where the overlap of the two members to be joined is in the range of 5 to 25mm, and preferably in the range of 5 to 15mm.

[0024] It is regarded as a definite advantage of the new method that it can be performed under outdoor circumstances, e.g. on a construction site. According to the invention the heating of the pasty filler can be performed by waving a flame across the pre-assembled joint region until the pasty filler liquidize and flows.

[0025] In another embodiment the heating of the pasty filler can be performed by electrical resistance heating, whereas other heating methods, such as induction heating are also applicable. An advantage of this method of heating of the pasty filler is that it can be applied manually, e.g. at a construction site, as well as in an (semi-) automated manner in an assembling or pre-assembling line for the production of for example automotive components. A further advantage of this method is that the heat required to liquidize and to flow the pasty filler can be applied very locally and accurately, and further that the possible effect of discoloured joint members does not occur.

[0026] In a further aspect the invention consists in an assembly of a soldered aluminium or zinc-coated aluminium member to a ferrous or zinc-coated ferrous member containing in the joint an aluminium-zinc alloy with a liquidus temperature below 419°C and containing aluminium in a range of 1.5 to 18 wt.%, the balance being zinc and impurities, produced by the method in accordance with the invention.

[0027] In another aspect the invention also consists in the use of a pasty metal containing filler, comprising 60 to 80 wt.% of a mixture of powdered metals, said mixture mainly comprising an aluminium-zinc alloy with a liquidus temperature below 419°C and containing aluminium in a range of 1.5 to 18 wt.%, the balance being zinc and impurities, the pasty filler further comprising 40 to 20 wt.% of an inorganic, fluorides containing flux material, for joining aluminium or zinc-coated aluminium members to ferrous or to zinc-coated ferrous members.

[0028] The invention will now be explained by several non-limitative examples.

[0029] In a test two strips of non-coated aluminium of the AA3003-type and non-coated low-carbon steel were joined in air according to the new method. The overlap of the two strips was 10 mm. The assembly was heated to about 400°C by using a natural gas-air torch. The filler used comprised 70 wt.% of powdered zinc-aluminium alloy, with an aluminium content of 2 wt.%, balance essentially zinc. The resulting test piece was subjected to a tensile test in accordance with ASTM D1002-94, in which an average shear strength of the joint was found of 15 MPa.

[0030] In a second test two strips of zinc-coated aluminium of the AA3004-type and zinc-coated low-carbon steel were joined in air according to the new method using the same filler composition and method of heating as in the first test. The resulting test piece was subjected to a tensile test in accordance with ASTM D1002-94, in which an average shear strength of the joint was found of 14 MPa. This means that in many cases the joints are stronger than the aluminium base sheet material.

[0031] Even after subjecting the joined members to the Atmospheric Building Corrosion Test, as described by B. Boelen in the article "New Product Test: The Atmospheric Building Corrosion Test (ABC Test)", published on the occasion of the ECCA Autumn Congress in Brussels on 27-28 November 1995, for several months no corrosion of the joint was observed.

Claims

1. Method of joining an aluminium member or a zinc-coated aluminium member to a ferrous member or to a zinc-coated ferrous member while applying a pasty metal containing filler in the joint region and thereupon heating of the pasty filler and subsequently cooling of the joint region, whereby the pasty filler contains 60-80 wt.% of a mixture of powdered metals, said mixture mainly comprising an aluminium-zinc alloy with a liquidus temperature below 419°C and containing aluminium in a range of 1.5 to 18 wt.%, the balance being zinc and impurities, the pasty filler further comprising 40 to 20 wt.% of an inorganic, fluorides containing flux material, and whereby the heating of the pasty filler is performed at a temperature below 430°C.
2. Method according to claim 1, wherein the aluminium-zinc alloy contains aluminium in a range of 1.5 to 5.0 wt.%, and preferably in a range of 1.5 to 2.5 wt.%.
3. Method according to claim 1 or 2, wherein weight of the zinc coating of the zinc-coated aluminium members is from 10 to 300 g/m².
4. Method according to any one of claims 1 to 3, wherein the weight of the zinc coating of the zinc-coated ferrous members is from 40 to 250 g/m².
5. Method according to any one of claims 1 to 4, wherein the zinc coating of the zinc-coated aluminium members and/or zinc-coated ferrous members is obtained by electrolytic deposition.
6. Method according to any one of claims 1 to 5, wherein the pasty filler is applied between the members where the joint is to result.
7. Method according to any one of claims 1 to 6, wherein the heating of the pasty filler is performed by waving a flame across the pre-assembled joint until the pasty filler liquidize and flows.
8. Method according to any one of claims 1 to 6, wherein the heating of the pasty filler is performed by electrical resistance heating.
9. Assembly of a soldered aluminium or zinc-coated aluminium member to a ferrous or zinc-coated ferrous member containing in the joint an aluminium-zinc alloy with a liquidus temperature below 419°C and containing aluminium in a range of 1.5 to 18 wt.%, the balance being zinc and impurities, produced by a method in accordance with any one of claims 1 to 8.
10. Use of a pasty metal containing filler, comprising 60 to 80 wt.% of a mixture of powdered metals, said mixture mainly comprising an aluminium-zinc alloy with a liquidus temperature below 419°C and containing aluminium in a range of 1.5 to 18 wt.%, the balance being zinc and impurities, the filler further comprising 40 to 20 wt.% of an inorganic, fluorides containing flux material, for joining aluminium or zinc-coated aluminium members to ferrous or to zinc-coated ferrous members.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 1563

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y,D	US 5 322 205 A (KATO SHUICHIRO ET AL) 21 June 1994 (1994-06-21) * the whole document *	1,10	B23K35/28 B23K35/36 //C22C18/04
Y,D	EP 0 785 045 A (FUSION INC) 23 July 1997 (1997-07-23) * the whole document *	1,10	
A	CHEMICAL ABSTRACTS, vol. 99, no. 4, 25 July 1983 (1983-07-25) Columbus, Ohio, US; abstract no. 26683, OKAI, RIEI, JAPAN: "Solders for low-temperature application" XP002080302 * abstract * & JP 58 041692 A (OKAI, RIEI, JAPAN)		
A	US 5 690 271 A (DUDEL KLAUS) 25 November 1997 (1997-11-25)		TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	US 3 066 406 A (P.R. WHITE) 4 December 1962 (1962-12-04)		B23K
A	DE 91 01 303 U (E. MÜLLER ET AL) 25 April 1991 (1991-04-25)		
A,D	DE 946 405 C (VEB LEICHTMETALLWERK) 2 August 1956 (1956-08-02)		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 6 August 1999	Examiner Mollet, G
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 20 1563

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

06-08-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5322205 A	21-06-1994	JP 2083229 C	23-08-1996
		JP 5185217 A	27-07-1993
		JP 7112626 B	06-12-1995
EP 0785045 A	23-07-1997	AU 6811896 A	31-07-1997
		CA 2183135 A	23-07-1997
		JP 9201694 A	05-08-1997
JP 58041692 A	10-03-1983	NONE	
US 5690271 A	25-11-1997	DE 4339498 A	24-05-1995
		AT 161454 T	15-01-1998
		BR 9408168 A	26-08-1997
		DE 59404907 D	05-02-1998
		WO 9513902 A	26-05-1995
		EP 0732983 A	25-09-1996
		SI 732983 T	30-04-1998
US 3066406 A	04-12-1962	BE 571156 A	
		FR 1210220 A	07-03-1960
DE 9101303 U	25-04-1991	AT 112705 T	15-10-1994
		DE 59200604 D	17-11-1994
		EP 0498154 A	12-08-1992
		ES 2063532 T	01-01-1995
DE 946405 C		NONE	